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ELECTROCHEMICAL STUDIES OF SULFUR OXYCHLORIDES

FINAL REPORT

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MARCH 28, 1988

U.S. ARMY RESEARCH OFFICE

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DEPARTMENT OF CHEMISTRY
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FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The electrochemistry of thionyl chloride has been studied at glassy carbon electrodes in dimethylformamide with tetrabutylammonium hexafluorophosphate as supporting electrolyte. Techniques employed were normal and reverse pulse voltammetry, rotating ring-disk voltammetry, coulometry and NMR. The reactions taking place during the reduction of SOCl_2 in DMF are probably best represented by the solvation reaction, $\text{SOCl}_2 + 2\text{DMF} \rightleftharpoons \text{SO} \cdot 2\text{DMF} + 2\text{Cl}^-$ and the electrochemical reduction, $\text{SO} \cdot 2\text{DMF} + 2e^- \rightleftharpoons \text{SO}^- \cdot 2\text{DMF}$ where the product, SO^- , may be solvated by DMF and can be reoxidized back to the initial reactant.			
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STATEMENT OF PROBLEM

The goal of this research was to study the fundamental electrochemistry of thionyl and sulfuryl chlorides utilizing pulse voltammetric and other electrochemical techniques, and fourier transform spectroelectrochemistry. It had been proposed to study sulfuroxyhalides (1) as solutes in a non-aqueous solvent, (2) undiluted, employing lithium tetrachloroaluminate and (3) as a major component in a mixed solvent with other non-aqueous solvents.

However, due to significant problems associated with this research, only item (1) was carried to completion. A rather detailed study of the reduction of thionyl chloride in dimethylformamide was carried out. The results, summarized below, represent new and novel findings when compared and contrasted to past work in this area.

SUMMARY OF RESULTS

In the initial phases of this work, controlled potential coulometry and rotating ring-disk electrode voltammetry for the reduction of SOCl_2 were carried out at glassy carbon electrodes in N,N-dimethylformamide (DMF) with tetra-butylammonium hexafluorophosphate (TBAPF_6) as supporting electrolyte. Cyclic voltammetry showed only one reduction wave for SOCl_2 in DMF, as opposed to other reports which have indicated several reduction waves at platinum electrodes. During the initial phases of the electrolysis, coulometry yielded an n value of two electrons per molecule of SOCl_2 reduced. During the latter phase of electrolysis, a value of n greater than two was obtained, Figure



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1. Cyclic voltammetry on the solution during electrolysis showed the presence of additional electroactive products which formed as the electrolysis progressed (Figure 2). Normal pulse voltammetric analysis of solutions containing thionyl chloride showed two chloride ions formed in solution for each molecule of SOCl_2 added to solution or reduced (Figure 3). The two electron product of the reduction was examined by rotating ring-disk voltammetry (Figure 4). The product is reasonably stable in DMF, as indicated by both the results of the coulometry and by the ring-disk studies, and can be reoxidized irreversibly, also in a two-electron process, as shown by the results of Table I which present data for the ring collection efficiency, N , yielding a mean value $1/N$ of 2.74, compared to a theoretical value, based solely on the ring-disk geometry, of $1/N = 2.6$. Thus, thionyl chloride in DMF was found to reduce in a two electron process at a glassy carbon electrode and yield a product, "SO", which could be reoxidized, also in a two electron process.

In a second phase of the work, normal and reverse pulse voltammetry were used to investigate both the reduction and oxidation of SOCl_2 at glassy carbon electrodes in DMF with TBAPF_6 as supporting electrolyte and NMR spectroscopy was used to probe for specific interactions between SOCl_2 and DMF. NMR spectra and the quantitative treatment of normal and reverse pulse voltammograms gave evidence for the displacement of Cl^- in SOCl_2 by DMF. The addition of AgNO_3 to the solution was found to remove chloride; i.e., the oxidation wave observed which corresponds to chloride oxidation diminished, while the SOCl_2 reduction wave was not affected (Figure 5, Figure 6). NMR

spectra showed evidence of a specific interaction between SOCl_2 and DMF (Figure 7, Table II). The reactions taking place during the reduction of SOCl_2 in DMF are probably best represented by the solvation reaction,



and the electrochemical reduction,



where the product, "SO", may be solvated by DMF and can be reoxidized back to the initial reactant. Analysis of normal pulse voltammograms for the SO^{2+} reduction indicate that the rate-determining step is a one-electron transfer, and there is no evidence for an intermediate in the overall electroreduction to "SO". It appears that "SO" species reacts further in a following chemical reaction at long pulse times and high concentrations of SOCl_2 . The oxidations of both "SO" and 2Cl^- are irreversible and involve two electrons.

PUBLICATIONS

"The Cathodic Reduction of SOCl_2 in N,N-dimethyl Formamide. I. Controlled Potential Coulometry and Rotating Ring-Disk Electrode Voltammetry", Masanori Sakai, Janet Osteryoung and Robert A. Osteryoung, Journal of the Electrochemical Society, in press.

"Pulse Voltammetric and NMR Investigations of SOCl_2 in N,N-Dimethyl Formamide", Winston Go, Masanori Sakai, Thomas Zawodzinski, Janet Osteryoung and Robert A. Osteryoung, Journal of Physical Chemistry, in press.

(reprints of these papers and DD-1473's will be forwarded when received)

PARTICIPATING SCIENTIFIC PERSONNEL

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Table I The ratio $-i_{\text{disk}}/i_{\text{ring}}$ measured at various potentials and rotation rates of the electrode for various concentrations of SOCl_2 containing 0.3 M TBAPP_6 in DMF at 27°C

Rotation	0.3 M SOCl_2					0.8 M SOCl_2						
	E_d, V	-0.775	-0.825	-0.875	-0.925	-1.025	-0.75	-0.775	-0.825	-0.875	-0.925	-1.025
rate, rpm												
250		2.65	2.72	2.73	2.70	2.78	2.62	2.60	2.63	2.66	2.68	2.69
500		2.68	2.68	2.71	2.75	2.74	2.60	2.61	2.65	2.67	2.66	2.68
750		2.72	2.73	2.73	2.72	2.74	2.60	2.60	2.67	2.65	2.68	2.67
1000		2.68	2.69	2.71	2.77	2.75	2.62	2.62	2.65	2.67	2.69	2.62
1500		2.74	2.72	2.73	2.74	2.78	2.64	2.63	2.66	2.68	2.69	2.68
2000		2.71	2.75	2.74	2.75	2.77	2.61	2.67	2.67	2.69	2.70	2.60
3000		2.77	2.76	2.75	2.76	2.78	2.64	2.64	2.67	2.68	2.71	2.70
4000		2.76	2.79	2.79	2.78	2.78	2.63	2.64	2.66	2.69	2.71	2.70

Rotation	2 M SOCl_2					3 M SOCl_2							
	E_d, V	-0.750	-0.775	-0.825	-0.875	-0.925	-1.025	-0.750	-0.775	-0.825	-0.875	-0.925	-1.025
rate, rpm													
250		2.73	2.70	2.70	2.68	2.70	2.68	2.62	2.66	2.63	2.68	2.68	2.59
500		2.65	2.69	2.68	2.70	2.68	2.69	2.65	2.68	2.69	2.69	2.70	2.74
750		2.65	2.71	2.68	2.69	2.72	2.70	2.63	2.71	2.69	2.73	2.74	2.72
1000		2.70	2.71	2.68	2.69	2.72	2.70	2.68	2.71	2.74	2.74	2.74	2.77
1500		2.70	2.73	2.70	2.69	2.70	2.71	2.70	2.73	2.72	2.75	2.76	2.77
2000		2.71	2.67	2.69	2.70	2.70	2.71	2.73	2.80	2.74	2.79	2.79	2.78
3000		2.77	2.73	2.70	2.70	2.71	2.70	2.77	2.80	2.79	2.79	2.79	2.80
4000		2.75	2.72	2.68	2.69	2.73	2.73	2.78	2.84	2.84	2.81	2.80	2.83

TABLE II Summary of ^{17}O NMR Data for SOCl_2 in DMF.

C_{SOCl_2} (M)	Relative Intensities			Chemical Shift (ppm)		
	I_A/I_B	I_A/I_C	$(I_A/I_C)^0_{\text{calc.}}$	A	B	C
	—	—	—	—	—	—
0.5	-	10.5	11.9	423.4	-	323.0
1.0	2.22	6.1	5.5	432.7	316.8	308.0
2.0	1.99	2.4	2.2	435.8	316.7	308.1

⁰ assuming the DMF molecules are associated with each SOCl_2 molecule.

Figure Captions

Figure 1. Plot of rotating disk limiting current, i_d , vs. number of coulombs, Q , during the controlled potential reduction of 2mM SOCl_2 with 0.15M TBAPF_6 in DMF at 27°C.

Rotation rate of the electrode, 1000 rpm; scan rate, 1 mV s^{-1} .

○, -1.6 V; ●, -1.2 V; —, -0.7 V.

Figure 2. Cyclic voltammograms before and during controlled potential coulometry of 2 mM SOCl_2 in DMF with TBAPF_6 at 27°C. Scan rate, 100 mV s^{-1} .

a) before electrolysis; b) $n \sim 0.5(9\text{C})$; c) $n \sim 1.2(24\text{C})$; d) $n \sim 1.8(34\text{C})$;

(-----), background.

Figure 3. Normal pulse voltammograms of the oxidation of solutions containing a) 2 mM SOCl_2 ; b) 2 mM Cl^- ; c) 2 mM SOCl_2 and 2 mM Cl^- in DMF with 0.15 M TBAPF_6 at 27°C. Pulse width, 40 ms; step height, 25 mV; delay before pulse, 5 s; (-----), background.

Figure 4. Reduction of 2mM SOCl_2 at a glassy carbon disk electrode and corresponding oxidation current on the glassy carbon ring electrode at various rotation rates in DMF containing 0.15 M TBAPF_6 at 27°C. Ring potential: +0.7 V; Scan rate; 1 mV s^{-1} . Rotation rates given on curves.

Figure 5. Normal pulse voltammograms for the (i) oxidation, and (ii) reduction of 2 mM SOCl_2 0.15 M TBAPF_6 in DMF with added AgNO_3 . $E_i = -0.050$ V, $t_p = 50$ ms, $A = 0.071$ cm², $C_{\text{AgNO}_3} = 0$ (\circ), 1 (Δ), 2 (\square), 3 (\times), and 4 (∇) mM. $t_d = 5$ s, $t_p = 50$ ms.

Figure 6. Normal pulse voltammetry of 2 mM SOCl_2 0.15 M TBAPF_6 in DMF with added AgNO_3 : dependence of $|i_{\text{NP}}|$ for the oxidation (ϕ) and reduction (\circ) currents on the concentration of added AgNO_3 . The reduction currents are the peak currents. For the oxidation currents, slope = 0.066 ± 0.003 mA/mM, intercept = -0.252 ± 0.005 mA, $R = 0.998$.

Figure 7. NMR spectrum of ^{17}O for 2 M SOCl_2 in DMF. Peaks are labelled from the furthest to the least downfield as A, B, and C respectively.

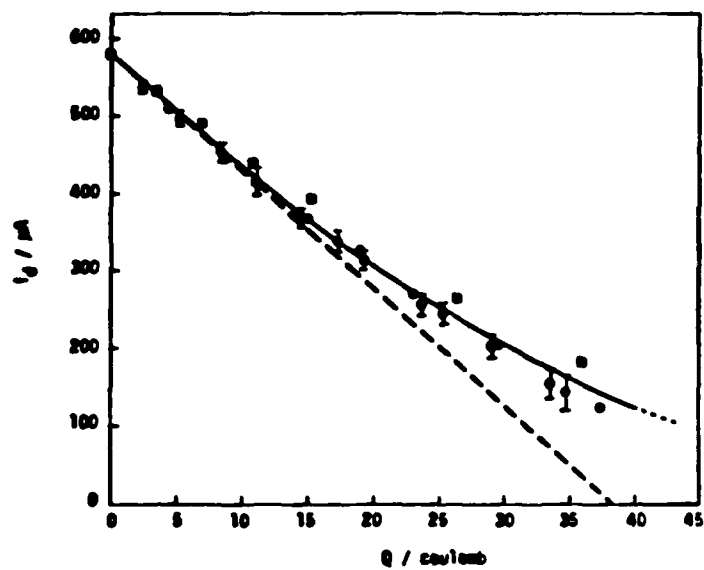


Figure 1

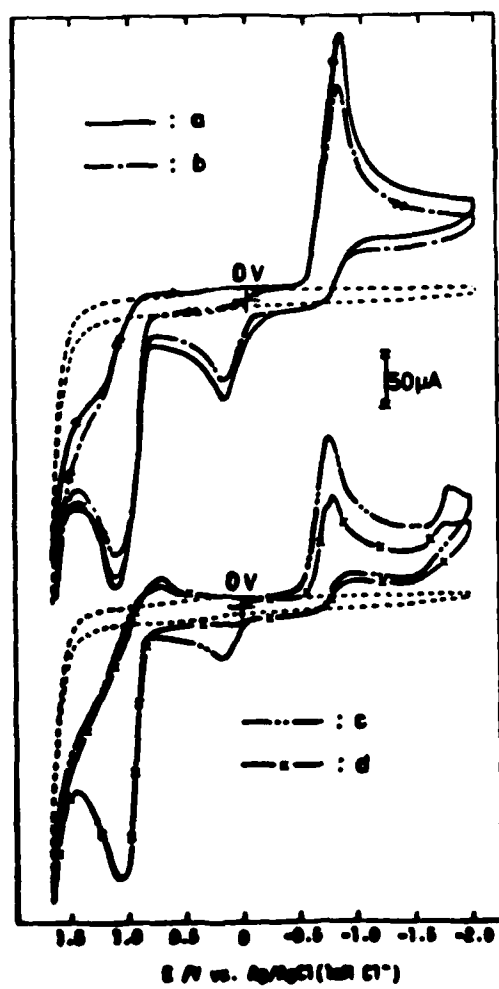


Figure 2

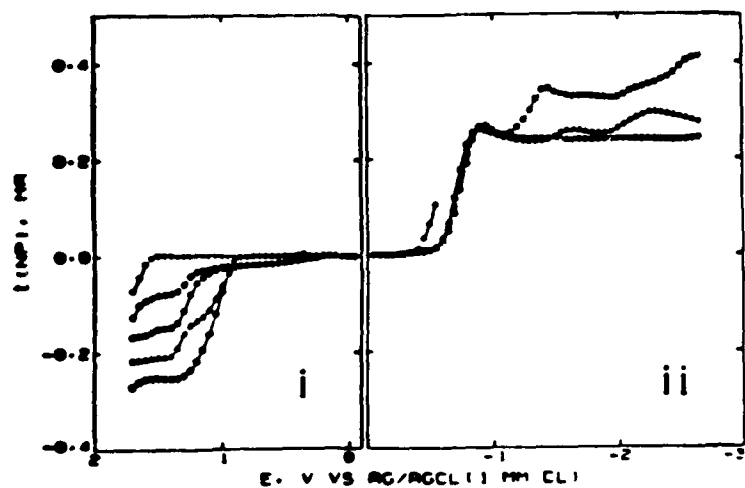


Figure 5

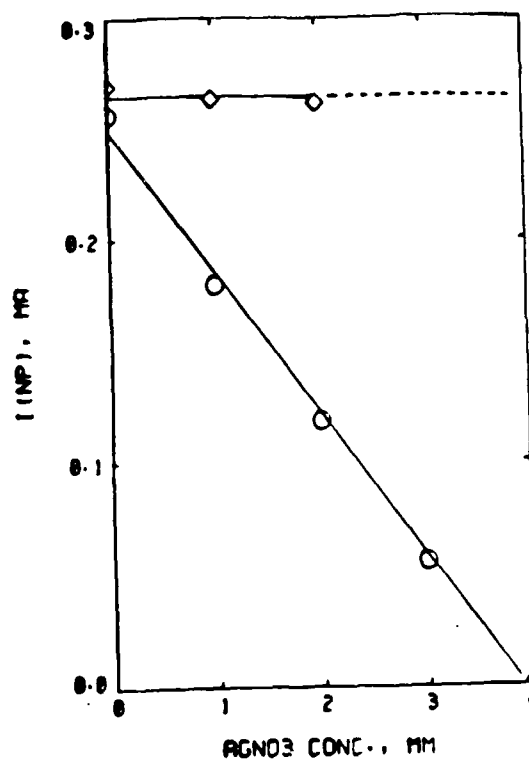


Figure 6

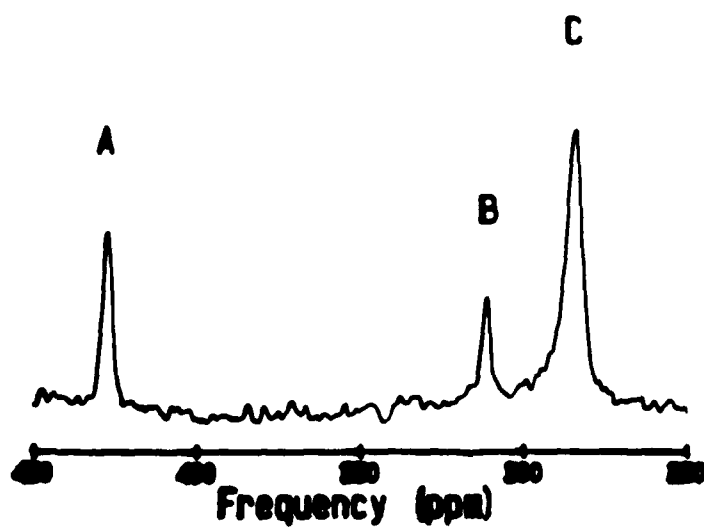


Figure 7

